

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
6 March 2003 (06.03.2003)

PCT

(10) International Publication Number
WO 03/018176 A1(51) International Patent Classification⁷: **B01D 53/32**, 53/92, 53/94, B01J 19/08, F01N 3/08, A61L 9/22

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/GB02/03843

(22) International Filing Date: 20 August 2002 (20.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

01 20775.2 25 August 2001 (25.08.2001) GB
01 28529.5 29 November 2001 (29.11.2001) GB

(71) Applicant (for all designated States except US): ACCENTUS PLC [GB/GB]; 329 Harwell, Didcot, Oxfordshire OX11 0QJ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HALL, Stephen, Ivor** [GB/GB]; 9 Blenheim Lane, Freeland, Oxford, Oxfordshire OX8 8AW (GB). **SHAWCROSS, James, Timothy** [GB/GB]; 27 Ticknell Piece Road, Charlbury, Oxfordshire OX7 3TN (GB). **INMAN, Michael** [GB/GB]; 2 Longfellow Drive, Abingdon, Oxfordshire OX14 5NU (GB). **McADAMS, Roy** [GB/GB]; 7 Upper Way Furlong, Didcot, Oxfordshire OX11 7ST (GB). **MORRIS, Keith** [GB/GB]; 15 Meadow Close, Grove, Wantage, Oxfordshire OX12 7NN (GB). **RAYBONE, David** [GB/GB]; 1 Talbot Cottages, Posse Way, Stow-on-the-Wold, Gloucester GL54 1DW (GB). **SEGAL, David, Leslie** [GB/GB]; 43 Foxborough Road, Radley, Abingdon, Oxfordshire OX14 3AB (GB). **STEDMAN, John** [GB/GB]; 7 Sutton Close, Abingdon, Oxfordshire OX14 1ER (GB).(74) Agents: **LOFTING, Marcus, John et al.**; c/o Accentus plc, Patents Dept., 329 Harwell, Didcot, Oxfordshire OX11 0QJ (GB).

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

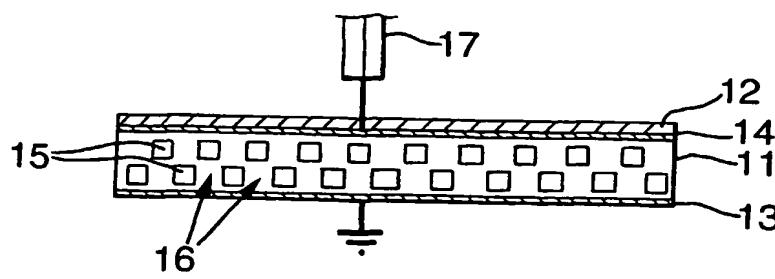
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

[Continued on next page]

(54) Title: NON-THERMAL PLASMA REACTOR



(57) Abstract: The space between parallel electrode plates (12, 13) of the reactor is dimensioned to make it possible to produce plasma at reasonable applied potential within the gas passages (15) of a monolithic substrate, such as a wallflow filter, in a slice (11) positioned between the electrode plates (12, 13).



- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Non-Thermal Plasma Reactor

The invention relates to a non-thermal plasma reactor and in one aspect to such a reactor for the treatment of exhaust gases from an internal combustion engine to remove or reduce pollutants such as carbonaceous particulates and oxides of nitrogen. In another aspect the invention relates to a non-thermal plasma reactor for the treatment of air which is to be re-circulated to the cabins in an aircraft.

Diesel particulate filters, known as wallflow filters, are used widely nowadays as particulate traps for diesel exhausts. Carbonaceous particulates, such as those found in diesel exhaust, are primarily of carbon (soot), but include hydrocarbons such as but not exclusively soluble organic fractions which may, for example, be adsorbed on the surface of soot particles. A typical cylindrical wallflow filter dimension is 5.66 inches (144 mm) diameter, 6 inches (152 mm) high with 100 cells per square inch (approx 15 per square centimetre). The wall thickness separating parallel rectangular channels running from end-face to end-face is around 17 thousandths of an inch (0.4 mm). The walls are porous, around 10 microns mean pore diameter. Alternate channels are blocked off at the ends so that the exhaust passes through the walls that trap particulates. As an example, such filters made of cordierite are sold under the name of Celcor by Corning Inc. Silicon carbide wallflow filters are also known. Flow through cordierite honeycomb filters in which all channels are open are used for supporting 3-way catalysts in the treatment of exhaust gases from gasoline engines. These monolithic materials, wallflow and flowthrough filters are widely accepted by the automotive industry as they meet the stringent

- 2 -

regulations on mechanical integrity when used on vehicles. Any material to be used in the treatment of exhaust gases from internal combustion engines must satisfy industry requirements on mechanical integrity.

5 Ceramic foams are also of interest for the treatment of exhaust emissions particularly in the treatment of carbonaceous particulates as they also are mechanically strong during use.

10 There is a requirement for improved methods of trapping and removing particulates from exhaust gas streams. One of the main challenges with achieving highly efficient filtration of particulates from gas streams is minimising the associated pressure drop across the filter

15 caused by the build up of particulates, by successfully regenerating the filter, before the filter clogs up. When a filter is incorporated into a non-thermal plasma reactor the latter can be powered continuously or intermittently when regeneration is required. A number

20 of reactor devices have been proposed employing non- thermal plasmas by themselves or in combination with catalyst materials, the so-called plasma-catalyst approach, for treatment of diesel exhaust emissions. The combination of a plasma with a substrate (for example, a

25 filter material) that acts as a particulate trap is known. Particulates trapped in this way can be oxidised by the plasma in the presence or absence of catalysts. Species implicated in the mechanism of oxidation are discussed in WO 01/30485 and the article by Thomas et al,

30 'Non-thermal Plasma Aftertreatment of Particulates - Theoretical Limits and Impact on Reactor Design', SAE 2000-01-1926 and include O, OH, O₃, NO₂, NO_x and electronically excited species. The plasma catalyst approach can also be used for the removal of nitrogen

35 oxides by selective catalytic reduction. Examples of the

use of this plasma catalyst approach are described in WO 00/43102, WO 00/71866 and in the international patent application PCT/GB02/01229.

5 It has been demonstrated that non-thermal plasmas can be generated when the substrate material contained between electrodes is in the form, for example, of spheres, for example in a packed bed reactor such as a ferroelectric bed reactor or in a dielectric barrier
10 reactor that contains for example spherical dielectric material such as alumina beads. Other forms of substrate material have been proposed such as a ceramic meshes, fragments, fibres or the like and these are described in WO 01/59270 and WO 00/51714. The existence of narrow
15 gaps, which may be referred to as microgaps, between substrate components of dielectric material in spherical form facilitates plasma formation, the plasma being initiated in the microgaps and expanding to fill wider gaps nearby. A similar effect can occur where the bed
20 comprises beads or pellets of shapes other than spherical. It has been suggested that such spheres, beads, or pellets, or the like could be replaced with monolithic foams, or honeycomb substrates. However, the absence of microgaps in such monolithic substrate
25 configurations means that in practice it is very difficult to generate plasma in the open channels, which they contain.

We have found unexpectedly that it is possible by
30 choice of reactor structural configuration and a specified relationship between electrode spacing and the peak applied voltage to cause plasma formation in such monolithic substrate configurations at reasonable applied excitation voltages and the invention is based upon this
35 discovery.

- 4 -

According to the invention, in one of its aspects, there is provided a method of manufacturing a non-thermal plasma reactor for the treatment of a gaseous medium comprising a monolithic substrate of dielectric material having gas passages therethrough, means for constraining gaseous medium to flow through the passages of the substrate, at least one pair of electrodes spaced apart with said monolithic substrate between them, at least one of the electrodes having its entire surface which faces the other electrode in intimate contact with a layer of dielectric barrier material, wherein the parameters of the monolithic substrate and dielectric barrier are chosen in relation to the required minimum peak voltage V_i for producing a non-thermal plasma in gas within the said gas passages in accordance with the relationship given by Equation 1 herein.

In Equation 1 " V_i " is the said required minimum peak voltage needed to be applied across the electrodes in order to generate the required V_{plasma} , where V_{plasma} is the peak voltage required to initiate a plasma discharge within the open area of a single gas passage of the monolithic substrate and is determined by the electrical characteristics of the gas in the gas passage, and the said parameters are defined as follows:

N is the height of a section of the monolithic substrate in terms of the number of gas passages contained within that height.

I_{ss} , which is given by Equation 2, is the ratio of current in an open gas passage area of monolithic substrate divided by the combined current in two vertical walls of the monolithic substrate material which define the sides of the gas passage. In order to limit power

- 5 -

loss in these walls this ratio should be not less than 1.0. To maximise plasma power this ratio I_{ss} should be as high as possible.

5 P_c is the transverse pitch of the gas passages, assumed to be square in cross section, and the pitch P_c is measured from the mid point of one side wall of a gas passage to the mid point of the opposite side wall.

10 T_w is the thickness of the side walls of the gas passages.

15 H_o is the width and height of the cross sectional dimensions of the open area (where plasma is formed) of a gas passage.

L_c is the length (at right angles to the width and height) of a gas passage.

20 ρ_c is the resistivity of the monolithic substrate material.

25 C_{sa} is the capacitance per unit surface area of the dielectric barrier.

ϵ_0 is the permittivity of vacuum.

ϵ_a is the relative permittivity of gas in the gas passage (eg exhaust gas).

30 ϵ_{c0} is the relative permittivity of the monolithic substrate material.

35 C_c is the combined capacitance of the two side wall columns.

- 6 -

$$C_{bc} := C_{sa} T_w L_c$$

5 Cs is the capacitance of each individual wall component
forming the top and bottom of a gas passage.

$$C_s := \epsilon_0 \cdot \epsilon_0 \cdot H_0 \cdot L_c \cdot \frac{2}{T_w}$$

10 Co is the capacitance of the open area of a gas passage
(in the absence of plasma).

$$C_o := \epsilon_0 \cdot \epsilon_a \cdot L_c$$

15 ω is the frequency of the applied alternating voltage in
units of radians per second.

j is the imaginary operator.

Rc is the resistance of each individual side wall column.

20

$$R_c := \frac{2\rho c H_0}{T_w L_c}$$

Ro is the resistance of the gas within the open area of a
gas passage.

25

The "required minimum peak voltage Vi" is a design
requirement for the reactor system which may be
determined by the available power supply system or what
is a practical power supply system. In general it will be
30 desirable for this to be as low as possible whilst
meeting the requirement to generate a non-thermal plasma.
In accordance with the invention key parameters for the

- 7 -

EQUATION 1

$$V_i := V_{\text{plasma}} \cdot N \cdot \left[1 + \left[\frac{1}{\left[\frac{\omega \cdot \left[\epsilon_{c0} \cdot \epsilon_0 \cdot (P_c - T_w) \cdot L_c \cdot \frac{2}{T_w} \right] \cdot I_j}{2} + \frac{1}{2 \cdot \left[\rho_c \cdot \frac{T_w}{2} \cdot \frac{1}{(P_c - T_w) \cdot L_c} \right]} \right]} + \frac{1}{\omega \cdot N \cdot [C_{sa} \cdot (P_c - T_w) \cdot L_c] \cdot I_j} \cdot \left(\omega \cdot C_o \cdot I_j + \frac{1}{R_o} \right) \right] \right]$$

EQUATION 2

$$I_{SS} = \frac{\frac{\omega \cdot (\epsilon_0 \cdot \epsilon_a \cdot R_o \cdot L_c \cdot \frac{1}{H_o}) \cdot I_j + \frac{1}{R_o}}{1 + \left[\frac{1}{\left(\frac{1}{(\omega \cdot 2 \cdot C_c \cdot I_j + \frac{2}{R_c}) \cdot I_j} + \frac{1}{\omega \cdot (C_{sa} \cdot T_w \cdot L_c) \cdot I_j} \right)} + \frac{1}{\left[\frac{\omega \cdot [C_{sa} \cdot T_w \cdot L_c] \cdot I_j}{\omega \cdot 2 \cdot C_c \cdot I_j + \frac{2}{R_c}} + \frac{1}{\omega \cdot (C_{sa} \cdot T_w \cdot L_c) \cdot I_j} \right]} + \frac{1}{2 \cdot \left[\rho_c \cdot \frac{T_w}{2} \cdot \frac{1}{(P_c - T_w) \cdot L_c} \right]} \right]} + \frac{1}{\omega \cdot [C_{sa} \cdot (P_c - T_w) \cdot L_c] \cdot I_j}}$$

specification of the electrode configuration associated with a monolithic substrate such as a wallflow filter are determined for a chosen peak voltage.

5 According to the invention, in another of its aspects, there is provided a non-thermal plasma reactor for the treatment of a gaseous medium comprising a monolithic substrate of dielectric material having gas passages therethrough, means for constraining gaseous
10 medium to flow through the passages of the substrate, at least one pair of electrodes spaced apart with said monolithic substrate between them, at least one of the electrodes having its entire surface which faces the other electrode in intimate contact with a layer of
15 dielectric barrier material, wherein, to reduce the minimum peak voltage required for producing a plasma in gas within the said gas passages below 30 kilovolts, the thickness of monolithic substrate between the electrodes is not greater than 11 mm. In a preferred arrangement,
20 in order to reduce the minimum peak voltage required for producing a plasma in gas within the said gas passages below 10 kilovolts, the thickness of monolithic substrate between the electrodes is not greater than 6 mm.

25 Preferably, the monolithic substrate comprises a ceramic, preferably cordierite, wallflow filter comprising an array of parallel rectangular passages separated by porous gas permeable walls, half of the passages being closed at one end and the other half of
30 the passages being closed at the other end such that adjacent passages are respectively closed at opposite ends, whereby gaseous medium entering the open passages at one end is forced to pass through the permeable walls to escape via passages which are open at the other end.

- 9 -

Alternatively, the monolithic substrate may comprise a ceramic honeycomb that can be of the flowthrough type or open pore foam, which may also be of cordierite.

However, the wallflow filter or honeycomb or open pore
5 foam may alternatively be fabricated from silicon carbide. The foam may a reticulated one or made by a gel casting process. The monolithic substrate may be fabricated from other materials including ceramic materials such as alumina.

10

A plasma reactor as aforesaid has application also for the treatment of air to be re-circulated to the cabins in an aircraft. There is a requirement to remove organisms such as bacteria, viruses, spores as well as
15 other particulate material that may be in the re-circulated air supply within aircraft cabins.
Particulate material, which may be antigenic, can include degradation products from aircraft furnishings, dust-mite faeces and degradation products of human tissue such as
20 dandruff. There is also an appreciation that it is necessary to remove odours that can occur periodically in the cabin. Also non-odorous gases present in the cabin may require removal. Examples of these gases are refrigerants, hydrocarbons, carbon monoxide, carbon
25 dioxide and ozone.

For this purpose the monolithic substrate, wallflow filter or honeycomb, preferably comprises or is coated with a molecular sieve or zeolite material which acts to
30 adsorb odorous gases. Alternatively, or additionally, gas passages of the monolithic substrate are packed with porous adsorbent material. Separate gas passages may contain different adsorbents or a combination of different adsorbents may be packed together into one,
35 some or all of the gas passages.

-10-

The material of the monolithic substrate and adsorbent packed into its gas passages will also serve to trap particulates and the efficiency of such trapping of particulates is enhanced by the presence of an electric field which promotes electrostatic trapping. Further enhancement of particulate trapping is provided by incorporating a fibrous material in the gas passages of the monolithic substrate, wallflow filter or honeycomb. For example, a fibre having a diameter of the order of 0.1 micron will electrostatically trap microorganisms 0.3 microns in diameter.

Specific constructions of reactor embodying the invention will now be described by way of example and 15 with reference to the drawings filed herewith, in which:

Figure 1 is a diagrammatic part cross-sectional view of a first embodiment,

20 Figure 2 is a diagrammatic part cross-sectional view of a second embodiment,

Figure 3 is a graph showing experimental results using a reactor such as is shown in Figure 1, and

25 Figure 4 is a diagrammatic part cross-sectional view of a third embodiment.

Referring to Figure 1, to facilitate the description 30 there is shown in end view a rectangular slice 11 from a cordierite wallflow filter sandwiched between a pair of parallel plate electrodes 12,13 shown in cross-section. The parallel plate electrodes 12,13 have a rectangular surface area corresponding to the dimensions of the sides 35 of the rectangular slice 11 of wallflow filter to which the electrodes are applied. In this example, a single

-11-

layer of dielectric barrier material between the electrode plates 12, 13 is provided by a thin film layer 14 of alumina in contact with the high voltage electrode plate 12. The entire surface of electrode plate 12 facing earthed electrode 13 is covered by the dielectric barrier layer 14, which is also in intimate contact with the rectangular slice 11 of wallflow filter. A thin film layer thickness of 1 mm is a convenient thickness.

10 Open ends of gas passages in the wallflow filter can be seen at 15 in Figure 1. Adjacent gas passages at 16 are closed at the end seen in Figure 1, but open at the opposite end. A high voltage lead for applying potential to electrode plate 12 is illustrated at 17.

15

The thickness of the rectangular slice 11 corresponds to the thickness of two rows of gas passages in a wallflow filter of the type mentioned above, thus representing a separation between the electrode plates 12, 13 of slightly less than 6 mm. For such an embodiment, we have found plasma is generated in all of the gas passages when an alternating or pulsed voltage at a peak level of 9 kilovolts is applied. A cell density of 100 cells per square inch and wall thickness of around 25 0.4 mm are convenient parameters for the substrate material.

If the thickness of the rectangular slice 11 is increased, higher voltage is required and, above a certain thickness, it becomes effectively impossible to establish plasma in the gas passages or such high peak voltages are required that they are not of practical use. However, we have demonstrated plasma generation with the thickness of the rectangular slice 11 corresponding to 4 rows of gas passages, which represents a spacing between the electrode plates 12, 13 of slightly less than 11 mm.

-12-

For this, a minimum peak voltage of an alternating or pulsed supply of 30 kilovolts was required.

Figure 2 illustrates an arrangement for providing a reactor with an increased gas flow capacity. Components which correspond with those shown in Figure 1 are referenced with the same reference numerals. The reactor of Figure 2 effectively corresponds to a stacked array of reactors of the form shown in Figure 1. In this example, four rectangular slices 11a, 11b, 11c, 11d are positioned between electrode plates 12a, 12b, 12c and 13a, 13b. The earthed electrode plates 13a, 13b are midway between the high voltage electrode plates 12a, 12b and 12b, 12c respectively. A high voltage lead for applying potential to the electrode plates 12a, 12b, 12c is illustrated at 17a. In this example, again only a single dielectric barrier layer is provided between the respective pairs of electrode plates. The respective dielectric barrier layers are shown at 14a, 14b, 14c, and 14d, the central high voltage electrode plate 12b having a dielectric barrier layer on both surfaces.

The reactors of these examples are particularly useful for the treatment of carbonaceous particulates including ultrafine material which is oxidised during its passage through the plasma and does not therefore have to be trapped in the walls of the wallflow filter, which would demand an impractically small pore size. Larger particulates are trapped and thus held for a longer residence time for exposure to the plasma for complete oxidation.

The compact form of the reactors and low voltage operation are particularly suitable for use in vehicle applications for treatment of the exhaust gases from internal combustion engines.

-13-

This is illustrated in the results of an experiment shown Figure 3. Exhaust from a diesel Genset was passed through a reactor similar to that shown in Figure 1. The reactor comprised a cordierite wall flow filter with 100 5 cells per square inch, three rows high about 70 mm wide and 50 mm in length sandwiched between plate electrodes, only one of which was provided with a surface layer dielectric barrier.

10 Soot in the exhaust is trapped in the filter of the reactor which was operated for the first six hours without any applied voltage (no plasma). The graph of Figure 3 shows pressure drop in millibars as ordinate against time as abscissa. The accumulation of soot on 15 the filter causes the increase seen in pressure drop during the first six hours operation up to the point marked "A". At this point "A" generation of non-thermal plasma in the reactor was initiated leading to a rapid fall in pressure drop consequent upon the oxidation of 20 the soot by the non-thermal plasma. The plasma was switched off at point "B" and accumulation of soot leads again to rising pressure drop until point "C", when the generation of non-thermal plasma was again initiated. The experiment finished at point "D".

25 It may be required to have a plasma generated in the reactor continuously, in order, for example, to oxidise ultrafine particulates which, not being trapped by the filter, would otherwise escape from the reactor.

30 However, where continuous generation of plasma is not required, intermittent operation such as demonstrated in Figure 3 can be achieved automatically by use of a pressure drop sensor which switches on the plasma when the pressure drop reaches a preset level and then 35 switches it off again when the pressure drop has fallen to a (lower) preset level.

-14-

Cordierite wallflow filters come in a range of cell geometries with defined cell pitch, (cells per square inch) and wall thickness. Examples of currently available wall flow filters are: 100 cpsi 0.43 mm wall thickness
5 (as mentioned above), 200 cpsi 0.31 mm wall thickness and 300 cpsi 0.31 mm wall thickness.

Generation of non thermal plasma within the open area of cordierite monolithic wallflow filter is
10 extremely difficult due to the physical construction of the monolith. Displacement currents flowing in the monolith structure as a result of applied high AC or pulsed voltages will flow through the open cell area and cordierite walls parallel to the direction of electric
15 field. The displacement currents flowing in the cordierite walls do not contribute to plasma formation and hence reduce the overall plasma generation efficiency. It is therefore prudent to minimise wall currents in order to maximise current flow in the open
20 cell area where plasma is generated, and thus improve the efficiency with which the applied electrical energy is transferred into the plasma.

Displacement currents are a function of the
25 magnitude of the applied AC or pulsed voltage and the physical properties of the cordierite material, including its resistivity and dielectric constant. For given properties we have calculated the effect of wall thickness on wall currents and plasma currents.
30

The resistivity and relative dielectric constant of a 100 cpsi cordierite wall flow filter as measured is around 2.5×10^9 ohm cm and 5.8 respectively.

-15-

In our calculation we have assumed dry clean cordierite for which the high resistivity does not significantly contribute to the current flowing in the walls. It should be noted, however, that high humidity 5 and soot loading will greatly affect current flow and hence distribution of currents. This characteristic is difficult to quantify as it will vary with time and operating conditions.

Our calculations have shown, not unexpectedly, that the current in the air gap is maximum when the ratio of cordierite wall thickness to cell pitch is zero, i.e. infinitely thin wall, and is the ideal condition for plasma generation within the open cell area. More 15 usefully, our calculation shows the way in which the current in the air gap decreases rapidly as the wall thickness increases.

Taking the upper acceptable limit of wall thickness 20 as that which results in equal currents in the open area (ie through the plasma) and the wall, our calculation shows this occurs for a wall thickness to cell pitch ratio of approximately 0.17. For a 100 cpsi monolith cell pitch of 2.54 mm, this corresponds to a wall thickness of 25 0.43 mm; for a 200 cpsi monolith cell pitch of 1.8 mm, this corresponds to a wall thickness of 0.31 mm. These dimensions are equal to the wall thickness found in existing manufactured monoliths, which are thus just able to meet the minimum efficiency requirement implied by the 30 limit we have set.

A preferred current distribution would be say 0.8 within the open cell area and 0.2 within the walls, however the very thin wall thickness required, (wall 35 thickness to cell pitch ratio of approximately 0.05), would be extremely difficult to manufacture.

-16-

A solution to the problem of achieving this required ratio would be to maintain the present wall thickness and cell height dimensions and to increase the width of the cell pitch so as to form rectangular shaped cells rather than the present square shaped cells.

Alternatively improved current distribution can be achieved if the dielectric constant of the material from which the wallflow filter is constructed can be reduced. 10 Or, desirably, both the cell width could be increased and the dielectric constant reduced.

Monolithic wallflow filters made from silicon carbide are produced by Ibiden Europa. Such filters are 15 described in an article by K.Ohno et al "Characterisation of SiC-DPF for passenger car" (SAE 2000-01-0185). The filter configuration is similar to that described above for cordierite and such silicon carbide filters provide an alternative to cordierite for use in accordance with 20 the present invention. The silicon carbide filters as manufactured are formed with a silicon carbide ceramic sealing skin around the sides of the filter. By modifying the manufacturing process so that this sealing skin (which has a high electrical resistivity), whilst 25 remaining non-porous, has a thickness of the order of 1 mm, the resultant sealing skin could serve as a dielectric barrier for an electrode plate secured thereon. A pair of opposed electrodes positioned on the sealing skin on opposite sides of the filter may be 30 provided by screen printing. In this way a compact non-thermal plasma reactor is produced with relatively few components and uniform thermal expansion characteristics.

It will be appreciated that electrodes for the 35 reactor may be provided in a variety of different ways. Rather than providing continuous plate electrodes

-17-

extending along the full length of the sides of the reactor, the plates may be broken up into two or more separated electrode plates. Electrical power need not necessarily be supplied to all such separated electrode 5 plates simultaneously, and but it may be applied sequentially in response to detection of preset levels of pressure drop. In this way, the electrical power supplied can be matched to the need for soot removal to regenerate the filter.

10

Figure 4 illustrates a reactor similar to that shown in Figure 2, but with electrodes provided by rods 21 each of which is encased, for example by plasma spraying, with a dielectric coating 22. The rods are received within 15 alternate channels in rows referenced 23, 24, 25, 26 of the wallflow filter monolith. This provides a variety of options for applying alternating or pulsed voltage potentials across the intervening body of the filter. For example, the rods in rows 24, 26 may be held at earth 20 potential and the alternating or pulsed high-voltage potential applied to the rods in rows 23, 26. Alternatively, a phased alternating supply may be connected with the 0° phase on row 23, the 120° phase on row 24 and the 240° phase on row 25.

25

The wallflow filter material can conveniently contain catalyst material for assisting in the removal of carbonaceous material or for treatment of nitrogen oxides or for treatment of both. The plasma can be used solely 30 for treatment of carbonaceous material. It can also be used for the combined treatment of particulate material and nitrogen oxides through initial conversion of nitric oxide to nitrogen dioxide and the selective catalytic reduction of nitrogen dioxide. With an appropriate 35 catalyst, specifically a silver doped activated alumina, the reactor can also be used for selective catalytic

-18-

reduction of nitric oxide in exhaust gases without prior conversion of this oxide to nitrogen dioxide. The ability to contain catalyst material in the filter material makes for a compact design for treatment of
5 exhaust gases and is, in this respect at least, an advantage over the use of a separate compartment of catalytic material outside the plasma region of the reactor. The plasma can also be used for the simultaneous treatment of carbonaceous material and
10 nitrogen oxides through reaction of nitrogen oxides and the carbonaceous material.

Treatment to remove nitrogen oxides may be provided by a separate dedicated reactor downstream of the reactor
15 for filtration and removal of carbonaceous particulates. This downstream reactor may either provide the entire facility for nitrogen oxide removal or be simply to mop up any nitrogen oxides not removed by selective catalytic reduction carried out in the wallflow filter plasma
20 reactor. Residual nitrogen oxides to be mopped up can be nitric oxide produced from the reaction of nitrogen dioxide with carbonaceous material.

The downstream reactor may incorporate an adsorber
25 catalyst for removal of nitrogen oxides. An adsorber catalyst is a compound that adsorbs nitrogen oxides in particular nitric oxide to form a solid metal nitrate salt under lean operating conditions. Barium-containing compounds and other alkaline earth compounds act as
30 adsorber catalysts. Examples of such catalysts are barium-zeolites, barium-aluminas, barium-silica-aluminas and barium-containing inorganic phosphates. Barium nitrate is an example of a solid metal nitrate formed under lean operating conditions. A rich pulse in the
35 exhaust gases causes hydrocarbon to reduce the adsorbed nitrate species to nitrogen. The rich pulse of

-19-

hydrocarbon may be activated in a non-thermal plasma before contact with the adsorber catalyst material although unactivated hydrocarbon that has not passed through a plasma region can be used for contacting the 5 catalyst. The downstream reactor may also contain a catalyst for the selective catalytic reduction (SCR) of nitrogen oxides or combination of adsorber material and SCR material. These catalytic materials either alone or in combination can be used inside or outside of a plasma 10 region, may be mixed together for example as a mixed coating on a honeycomb filter or may be used in separate compartments in the downstream reactor.

The wallflow filter reactors of the foregoing 15 examples may be adapted for use as a filter for re-circulated aircraft cabin air. For this the wallflow filter is either fabricated from or coated with a molecular sieve or zeolite material for adsorbing odorous gases and, in addition, the gas passages may be packed 20 with porous adsorbents. (Note that materials for adsorbing odorous gases in recirculated aircraft cabin air are distinct from adsorber catalysts). The adsorbent materials are selected according to the gaseous species required to be adsorbed. As molecular sieves or 25 adsorbents such as activated carbon may be selective to particular gaseous species, a combination of adsorbents may be required. These may be combined together in one, some, or all of the gas passages of the wallflow filter, or different adsorbents may be accommodated in separate 30 gas passages.

Further, for improving the trapping efficiency of particulates, and particularly microorganisms, the gas passages include a packing of fibres. Fibre of diameter 35 of the order of 0.1 micron is capable of electrostatically trapping microorganisms of the order of 0.3

-20-

micron diameter. Examples of fibres that can be used in the gas passages are Saffil alumina, Nextel fibre produced by 3M, silicon carbide for example Nicalon and Tyranno as produced by Nippon Carbon and Ube Chemicals.

5 Saffil is a porous ceramic fibre. Non-porous fibres such as glass fibres can also be used as can melt-blown aluminosilicate fibres such as Kaowool. Other fibres can be used providing they are thermally stable at the operating temperature of the plasma, typically 200°C.

10 Fibres can consist of a number of smaller diameter fibres wound together at the manufacturing stage to form a thread, or woven into mats or meshes.

Gas passages in the wallflow filter can also be packed with fine fibre stainless steel filter material or non-metallic thread or a combination of one or more of these materials with one or more adsorbent materials.

A filter containing adsorbent material and/or fibrous material as described above is capable of trapping organisms, particulate matter and adsorbing gases. It is thus has usefulness for both the automotive and aircraft air treatment applications. The plasma destroys the organisms and particulate matter but may not destroy the adsorbed gases. The filter can be treated at an aircraft destination to remove the adsorbed gases either in situ or after removal from the aircraft if the plasma has not destroyed adsorbed species on the adsorbent. However, it is noted that the physical state of an adsorbed species is similar to a condensed liquid which may therefore be expected to aid destruction of adsorbate by the plasma.

The established structural integrity of wallflow filters is an advantageous feature of the reactors of the

-21-

foregoing examples for both automotive and aircraft applications.

The invention is not restricted to the details of
5 the foregoing examples. For instance, dielectric barrier layers 14, 14a, 14b, 14c, 14d can be provided on all facing electrode surfaces, that is on the upper surface of electrode plate 13 of the embodiment shown in Figure 1 and both surfaces of the electrode plates 13a, 13b of the
10 embodiment shown in Figure 2. The dielectric barrier layers need not necessarily be of alumina but may be of any suitable dielectric material.

The striking potential of the plasma can be reduced
15 by forming metal contacts in at least one gas passage of the monolith, that is by forming a triple junction, for example by placing a metallic rod in a gas passage in contact with the dielectric material of a wall of the gas passage.

20 For some applications it may be possible to fabricate the wallflow filter or other monolithic substrate from catalytic material, rather than incorporating catalytic material as an impregnation or
25 coating. In addition, the non-thermal plasma reactor described herein in which a filter material such as a wallflow monolith is contained within the plasma region may be combined with a high efficiency particulate air (HEPA) filter. In this combination the filter is placed
30 downstream of the reactor and is particularly useful when the reactor is used to kill microorganisms so that debris contained in the exhaust gases from the reactor is collected in the HEPA filter.

35 Application has been described for treatment of air recirculated to an aircraft cabin. It will be

-22-

appreciated that the wallflow filter reactor of the examples may equally well be used for treatment of air provided by any air circulation system, such as for a room or building, for example.

Claims

1. A non-thermal plasma reactor for the treatment of a gaseous medium comprising a monolithic substrate (11) of dielectric material having gas passages (15,16) therethrough, means for constraining gaseous medium to flow through the gas passages (15,16) of the substrate, at least one pair of electrodes (12,13;21) spaced apart with said monolithic substrate (11) between them, at least one of the electrodes (12,13;21) having its entire surface which faces the other electrode in intimate contact with a layer of dielectric barrier material (14;22), characterised in that, to reduce the minimum peak voltage required for producing a plasma in gas within the said gas passages below 30 kilovolts, the thickness of monolithic substrate (11) between the electrodes (12,13;21) is not greater than 11 mm.
2. A non-thermal plasma reactor as claimed in claim 1, further characterised in that, in order to reduce the minimum peak voltage required for producing a plasma in gas within the said gas passages below 10 kilovolts, the thickness of monolithic substrate (11) between the electrodes (12,13;21) is not greater than 6 mm.
3. A non-thermal plasma reactor as claimed in claim 1 or claim 2, further characterised in that the monolithic substrate (11) comprises a ceramic wallflow filter comprising an array of parallel rectangular passages (15,16) separated by porous gas permeable walls, half (15) of the passages being closed at one end and the other half (16) of the passages being closed at the other end such that adjacent passages are respectively closed at opposite ends, whereby gaseous medium entering the open passages at one end is forced to pass through the

-24-

permeable walls to escape via passages which are open at the other end.

4. A non-thermal plasma reactor as claimed in claim 3,
5 further characterised in that the ceramic wallflow filter
is fabricated from cordierite.

5. A non-thermal plasma reactor as claimed in any of
the preceding claims, further characterised in that the
10 monolithic substrate (11) comprises or contains catalytic
material for promoting reactions for removing unwanted
constituents of a gaseous medium passed through the
reactor.

15 6. A non-thermal plasma reactor as claimed in any of
the preceding claims for the treatment of air to be re-
circulated to the cabins in an aircraft, further
characterised in that the monolithic substrate (11)
comprises or is coated with a molecular sieve or zeolite
20 material which acts to adsorb odorous gases.

7. A non-thermal plasma reactor as claimed in any of
the preceding claims for the treatment of air to be re-
circulated to the cabins in an aircraft, further
25 characterised in that gas passages (15,16) of the
monolithic substrate (11) are packed with porous
adsorbent material.

8. A non-thermal plasma reactor as claimed in claim 7,
30 further characterised in that separate gas passages
(15,16) contain different adsorbents.

9. A non-thermal plasma reactor as claimed in claim 7,
further characterised in that a combination of different
35 adsorbents are packed together into one, some or all of
the gas passages (15,16).

-25-

10. A non-thermal plasma reactor as claimed in any of claims 6 to 9, further characterised in that a fibrous material is incorporated in the gas passages (15,16) of the monolithic substrate (11).

5

11. A non-thermal plasma reactor as claimed in claim 10, further characterised in that the fibrous material comprises fibre having a diameter of the order of 0.1 micron.

10

12. A method of manufacturing a non-thermal plasma reactor for the treatment of a gaseous medium comprising a monolithic substrate (11) of dielectric material having gas passages (15,16) therethrough, means for constraining 15 gaseous medium to flow through the passages (15,16) of the substrate (11), at least one pair of electrodes (12,13;21) spaced apart with said monolithic substrate (11) between them, at least one of the electrodes (12,13;21) having its entire surface which faces the 20 other electrode in intimate contact with a layer of dielectric barrier material (14;22), characterised in that the parameters of the monolithic substrate and dielectric barrier are chosen in relation to the required minimum peak voltage V_i for producing a non-thermal 25 plasma in gas within the said gas passages in accordance with the relationship given by Equation 1 herein.

1/2

Fig.1.

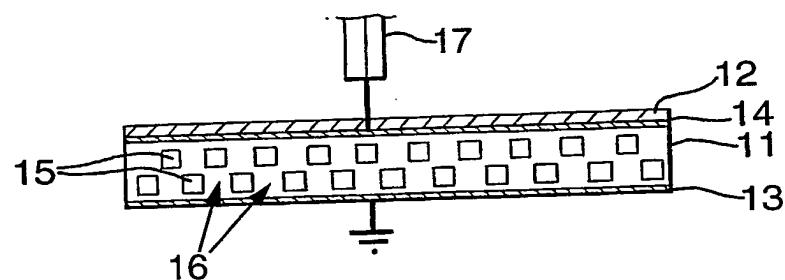
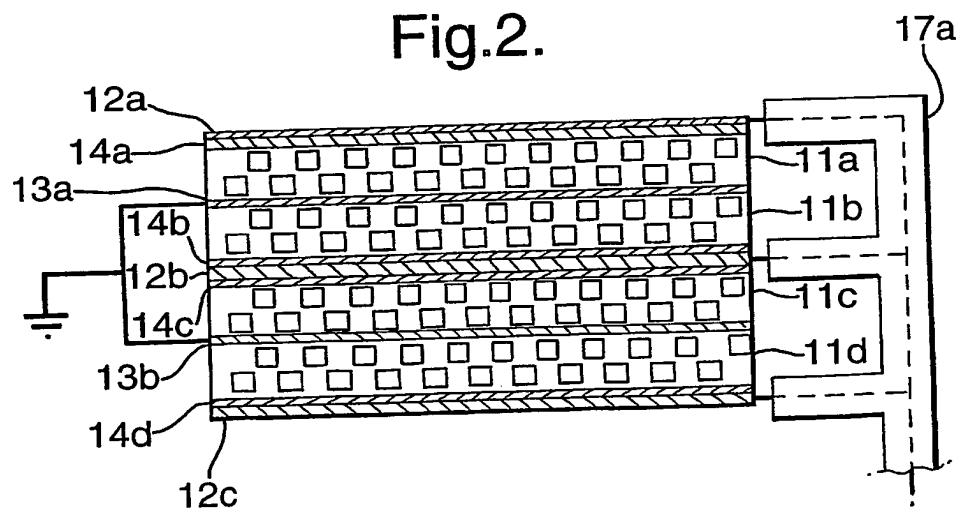


Fig.2.



2/2

Fig.3.

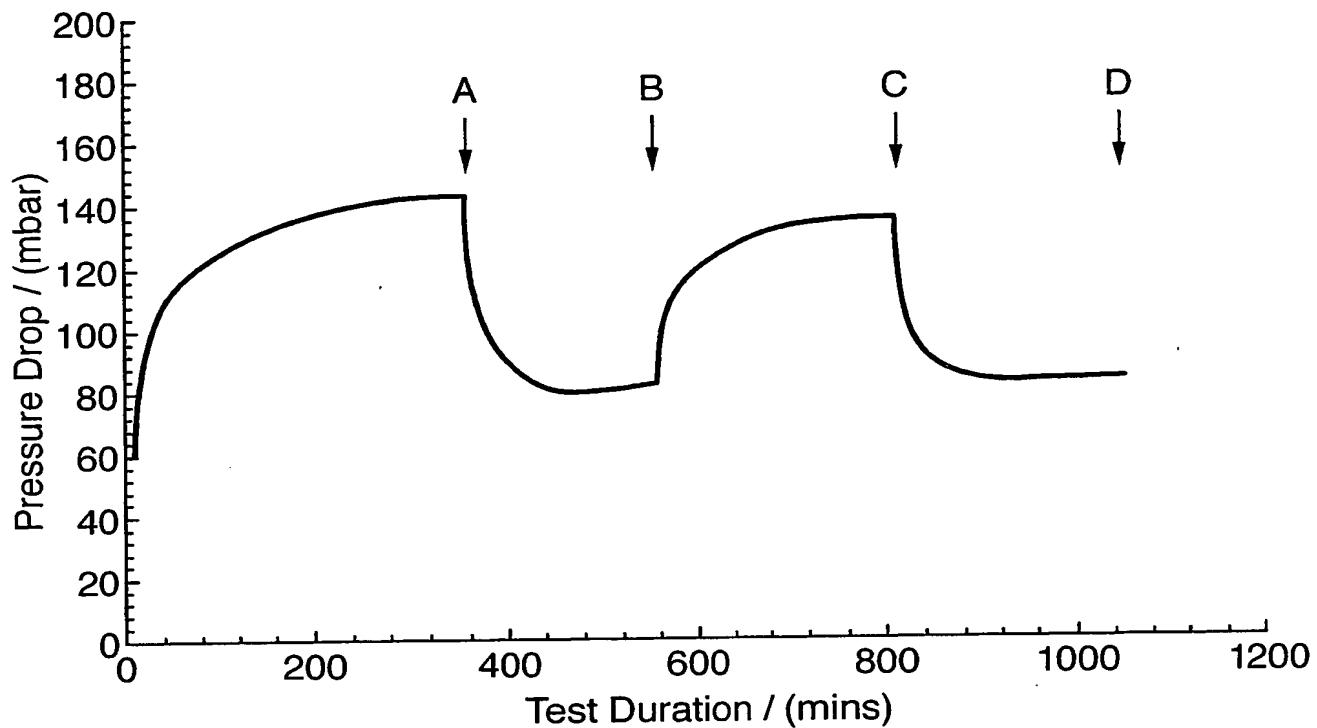
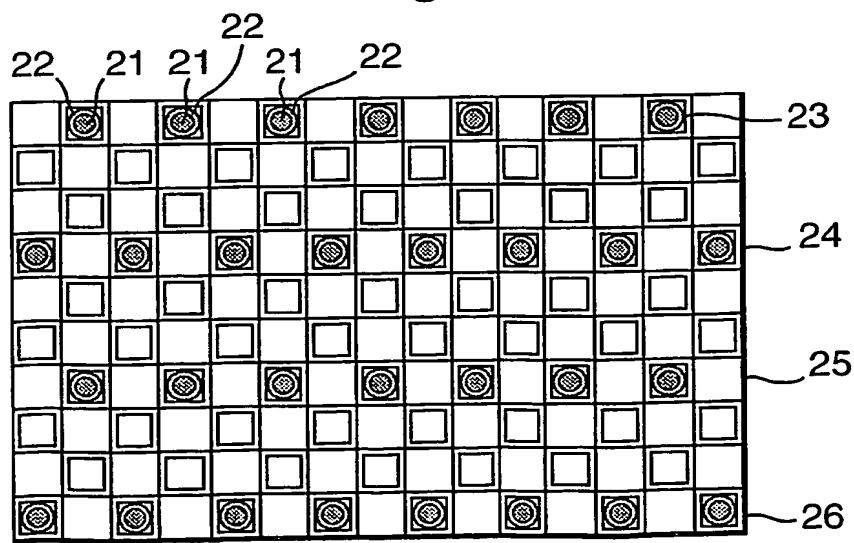


Fig.4.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 02/03843

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B01D53/32 B01D53/92 B01D53/94 B01J19/08 F01N3/08 A61L9/22				
--	--	--	--	--

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D B01J F01N A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 885 647 A (FLECK CARL MARIA PROF DR) 23 December 1998 (1998-12-23)	1,2,12
A	claims 1-7; figures 1,2	3-11
X	WO 92 00442 A (FLECK CARL M) 9 January 1992 (1992-01-09)	1,2,12
A	page 11, line 6 - line 26; claims 1-7; figure 4	3-11
X	DE 101 02 681 A (MITSUBISHI HEAVY IND LTD ;MITSUBISHI MOTORS CORP (JP)) 9 August 2001 (2001-08-09)	1,2,12
A	claims 1-6; figures 1-14	3-11
X	EP 1 086 740 A (ISHII SHOZO ;NGK INSULATORS LTD (JP)) 28 March 2001 (2001-03-28)	1,2,12
A	figures 20,21	3-11
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

& document member of the same patent family

Date of the actual completion of the international search

20 December 2002

Date of mailing of the international search report

10/01/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Kanoldt, W

INTERNATIONAL SEARCH REPORT

In	ational Application No
PCT/GB 02/03843	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 49278 A (ANDREWS PETER JAMES ;HALL STEPHEN IVOR (GB); SHAWCROSS JAMES TIMOT) 24 August 2000 (2000-08-24) figures 1-3 ---	1,2,12
A	---	3-11
X	WO 99 43419 A (ANDREWS PETER JAMES ;HALL STEPHEN IVOR (GB); SHAWCROSS JAMES TIMOT) 2 September 1999 (1999-09-02) figures 1-9 ---	1,2,12
A	---	3-11
X	WO 00 51714 A (INMAN MICHAEL ;AEA TECHNOLOGY PLC (GB)) 8 September 2000 (2000-09-08) cited in the application claims 1-23; figure 2 ---	1,2,12
A	---	3-11
X	WO 99 38603 A (AEA TECHNOLOGY PLC ;SEGAL DAVID LESLIE (GB)) 5 August 1999 (1999-08-05) claims 1,17; figure 1 ---	1,2,12
A	---	3-11
X	EP 1 023 935 A (DEGUSSA) 2 August 2000 (2000-08-02) claims 1-7; figure 8 ---	1,2,12
A	---	3-11
A	WO 01 34281 A (FLECK CARL M) 17 May 2001 (2001-05-17) figures 1-7 -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 02/03843

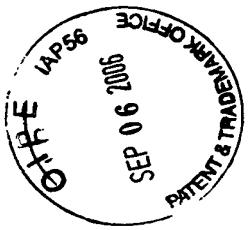
Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0885647	A	23-12-1998	AT 2330 U1 EP 0885647 A2	25-08-1998 23-12-1998
WO 9200442	A	09-01-1992	AT 395827 B WO 9200442 A1 AT 102290 T AU 647491 B2 AU 8006691 A BR 9106611 A CA 2086675 A1 CZ 9203965 A3 DE 59101116 D1 EP 0537219 A1 ES 2051125 T3 HU 67482 A2 KR 175062 B1 RU 2078952 C1 SK 396592 A3 US 5402639 A AT 168490 A	25-03-1993 09-01-1992 15-03-1994 24-03-1994 23-01-1992 01-06-1993 03-01-1992 15-09-1993 07-04-1994 21-04-1993 01-06-1994 28-04-1995 20-03-1999 10-05-1997 03-04-1996 04-04-1995 15-08-1992
DE 10102681	A	09-08-2001	JP 2001205039 A DE 10102681 A1 US 2001023589 A1	31-07-2001 09-08-2001 27-09-2001
EP 1086740	A	28-03-2001	JP 2001087620 A EP 1086740 A2	03-04-2001 28-03-2001
WO 0049278	A	24-08-2000	AT 226276 T AU 2448100 A DE 60000609 D1 EP 1153207 A1 WO 0049278 A1 JP 2002537510 T	15-11-2002 04-09-2000 21-11-2002 14-11-2001 24-08-2000 05-11-2002
WO 9943419	A	02-09-1999	AU 2535999 A EP 1058577 A1 WO 9943419 A1 JP 2002504421 T	15-09-1999 13-12-2000 02-09-1999 12-02-2002
WO 0051714	A	08-09-2000	AT 224762 T AU 2817400 A DE 60000510 D1 EP 1156866 A1 WO 0051714 A1 JP 2002538361 A	15-10-2002 21-09-2000 31-10-2002 28-11-2001 08-09-2000 12-11-2002
WO 9938603	A	05-08-1999	AU 2177399 A EP 1051234 A1 WO 9938603 A1 JP 2002501813 T US 2002034461 A1	16-08-1999 15-11-2000 05-08-1999 22-01-2002 21-03-2002
EP 1023935	A	02-08-2000	DE 19903533 A1 EP 1023935 A1 JP 2000271447 A US 2001002244 A1	10-08-2000 02-08-2000 03-10-2000 31-05-2001

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/GB 02/03843

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
WO 0134281	A 17-05-2001	AT AT WO AU EP	409653 B 189799 A 0134281 A1 1644001 A 1229992 A1	25-10-2002 15-02-2002 17-05-2001 06-06-2001 14-08-2002



THIS PAGE BLANK (USPTO)